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ELECTROCHEMICAL REACTIONS WITH BARE METAL SURFACES AND
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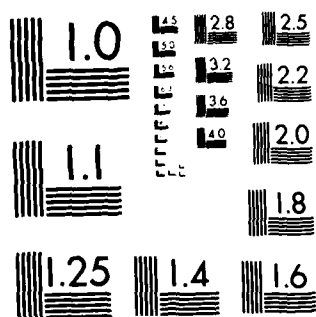
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ELECTROCHEMICAL REACTIONS WITH BARE METAL SURFACES
AND CORROSION FATIGUE CRACK GROWTH

by

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A TECHNIQUE FOR MEASURING THE KINETICS OF ELECTROCHEMICAL
REACTIONS WITH BARE METAL SURFACES

A. Alavi, C. D. Miller and R. P. Wei

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Abstract

To assist in the understanding of corrosion fatigue crack growth in aqueous environments, an in situ fracture technique for measuring the kinetics of electrochemical reactions with bare metal surfaces has been developed and evaluated. The experimental procedure and preliminary results, and the potential of this technique in advancing the understanding of corrosion fatigue are described and discussed.

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To assist in the understanding of corrosion fatigue crack growth in aqueous environments, an in situ fracture technique for measuring the kinetics of electrochemical reactions with bare metal surfaces has been developed and evaluated. The experimental procedure and preliminary results, and the potential of this technique in advancing the understanding of corrosion fatigue are described and discussed.

Introduction

To advance the understanding of the mechanism of corrosion fatigue, it is necessary to evaluate the electrochemical processes that occur at the crack tip. For this purpose, a simulation technique which facilitates the measurement of bare-metal reaction kinetics under controlled environmental conditions (namely, electrolyte composition and temperature) has been developed. In this paper the experimental procedure, preliminary test results, and a comparison of the reaction data with corrosion fatigue crack growth response are described and discussed.

Background

Transient electrochemical reactions that proceed on freshly exposed metal surfaces at the crack tip are important because these are believed to control crack growth in high strength steels exposed to aqueous environments.^{1,2} Newman³ reviewed the efforts at relating transient anodic processes on bare metal surfaces to environmentally assisted crack growth. Various attempts have been made to simulate the crack tip conditions, and to measure the reaction kinetics by monitoring the current transients that are induced when, by means of a mechanical process, bare metal is exposed to the environment. The principal difficulty has been associated with the creation of this highly reactive (and hence short-lived) bare surface in situ and in a manner that is reproducible.

Beck⁴ reviewed the techniques employed prior to 1975 for creating bare metal surfaces, and separated them into 5 major groups. They are as follows: (i) forming liquid metal droplets, (ii) scraping or scratching a surface, (iii) straining a wire, (vi) shearing a wire, and (v) rapid fracturing of a tensile specimen. A brief review of the techniques used since 1975 is given here to provide background for the proposed technique.

Foley and co-workers⁵⁻⁷ developed a continuous-scraping technique for measuring potential on bare aluminum alloy surfaces. In their technique, a rotating cylindrical electrode was scraped in a closed cell by a ceramic cutting tool. The working electrode surface was isolated from the electrolyte with Teflon except for the circular area which was exposed by the tool during the experiments.

A similar technique was described by Lees and Hoar⁸ for studying brass in Mattsson solutions. In their experiments, an annular scratch was made on the surface of a rotating disc working electrode, in solution, by a diamond stylus. The area of the scratched surface constituted only a tiny fraction of the working electrode surface. Furthermore, at any given time, the proportion of the scratch that remained bare depended on the nucleation and growth rates of the oxide and on the rotation speed of the working electrode. This technique was also applied by Ford et al.^{9,10} to the study of aluminum and by Burstein and Davies^{11,12} to iron. Because the oxide nucleation and growth rates on these metals are fast, these researchers modified the technique so that scratches could be generated on the rotating

discs by a brief contact (0.2 to 1.8 ms) with the diamond stylus. This technique was further employed to study the bare-surface reactions on gold¹³, silver^{14,15}, brass¹⁶ and copper¹⁷.

Newman et al. also used a scratching technique to simulate the crack-tip reactions associated with intergranular stress corrosion cracking of sensitized type 304 stainless steel in sodium thiosulfate solutions¹⁸⁻²⁰, and to study the pitting susceptibility of stainless steels in sulfate/thiosulfate electrolytes²¹. The alloy specimen was mounted on the base of a small open cell which contained the electrolyte, and the reference and counter electrodes, and was scratched manually with a diamond engraving pencil. The reproducibility of scratch area between successive experiments had been estimated to be about 15%¹⁸. In one study¹⁹, two other techniques were employed to expose bare metal surfaces. One involved the fracture of hydrogen-charged multi-notched strips of stainless steel by manually bending them in the electrolyte. In the other, smooth tensile specimens were immersed in the electrolyte contained in a small beaker, and strained in a servo-hydraulic machine under various load or displacement control. In these investigations¹⁸⁻²¹, electrolytes were exposed to air because deoxygenation was found to be unnecessary.

The straining electrode (metal wire) technique has received attention²²⁻²⁶, particularly by researchers in the area of stress corrosion cracking. Although rapid straining is useful for

exposing bare metal surfaces in situ, the amount of area created may vary depending on the ductility of the surface oxide.⁴

The authors believe that a successful technique should incorporate the following features: Firstly, bare surfaces having a controlled dimension should be exposed to the environment instantaneously rather than progressively. Secondly, the bare surface should be the only portion of the working electrode surface that is exposed to the electrolyte, so as to preclude extraneous reactions and the associated exchange of current with adjacent oxidized surfaces. Thirdly, the reaction cell should be closed so that the electrolyte composition (including oxygen content) can be controlled, or maintained constant. The in situ fracture technique described herein was designed with these considerations in mind. This technique is similar to that employed by Beck^{27,28} for studying the stress corrosion cracking of titanium alloys where epoxy-coated notched specimens were fractured by a drop-weight method in a closed Teflon cell.

Experimental Procedure

The procedure involved measurement of the equilibration galvanic current (or charge transfer) between the bare surfaces produced by in situ fracture of a notched round (5mm notch diameter) tensile specimen and an "oxidized" surface of the same material in the electrolyte. The specimen was fully isolated from the electrolyte with lacquer and Teflon heat-shrink tubing, so that only the fracture surfaces (with a total nominal area of 0.4 cm^2 for the two halves) would be exposed. The counter elec-

trodes (cathode) consisted of 4 rods of the same material which were situated concentrically around the test specimen in a 260 mL capacity Plexiglas cell (Figure 1). The counter electrodes were electrically connected to the specimen through a potentiostat operated as a zero-impedance ammeter. The cell was sealed with O-rings, and the nominal cathode-to-anode surface area ratio was 250:1. A Luggin probe, with its tip placed near to the specimen notch and leading to a saturated calomel electrode (SCE), was used to monitor potential.

For each experiment, the counter electrodes were first abraded with fine emery paper and degreased in an ultrasonic cleaner, and were then assembled into the corrosion cell. The sealed system was thoroughly flushed with nitrogen and filled with deaerated electrolyte at the selected test temperature, and was allowed to stabilize. The electrolyte temperature in the cell was monitored with a glass thermometer. The counter electrodes (cathode) were then "cleaned" by cathodically polarizing to -1000 mV (SCE) against an external platinum anode for five minutes, after which the cell electrolyte was flushed out with dry nitrogen and refilled. Fresh electrolyte was allowed to flow through the cell at 3 to 5 mL/s. Sufficient time was then given (5-10 minutes) to permit the system to re-stabilize, and to allow the counter electrodes to reach the free corrosion potential. This cathodic polarization pretreatment was found to result in a more reproducible surface condition on the cathode between successive runs.

Once the system had been stabilized and the free corrosion potential on the counter electrodes had been established, the specimen was loaded to fracture in a tensile testing machine. The current transient and the mixed potential following fracture were monitored and were recorded with the aid of a digital computer for analysis. Data were acquired at an initial interval of 0.01 s, and at 0.1 to 5 s thereafter.

The measured current transient represents the equilibration current between the freshly exposed fracture surfaces and the counter electrodes as the conditions at the fracture surfaces approach those of the counter electrodes. The mixed potential is the value between the separate, but electrically connected, surfaces and the saturated calomel reference electrode. No IR compensation was used in these initial experiments.

Results and Discussion

To test this technique, initial experiments were carried out on a W1 steel (composition in wt% : C 0.6-1.4, Mn 0.35 max, Si 0.35 max, Cr 0.20 max) in deaerated 0.6 M NaCl (pH 6.5). Representative current transients* and mixed potentials at 276, 296 and 313 K (3, 23 and 40 C) are shown in Figures 2 and 3. The current decayed rapidly at first, and then more gradually as complete equilibration was approached. The time to complete

*Because the area of the fracture surfaces is not precisely known, the actual current (and charge transfer) between the two halves of the fractured specimen and the counter electrodes is reported. Nominal current and charge densities can be readily obtained by dividing the respective values by the nominal fracture surface area (both halves) of 0.4 cm². The actual densities, however, will be lower on account of surface roughness.

equilibration was reduced with increasing temperature. The currents were reproducible to within $\pm 30\%$ in triplicate experiments. The free corrosion potentials, following the initial cathodic pretreatment at 276, 296 and 313 K (3, 23 and 40 C) were -765 ± 10 , -790 ± 10 , and -780 ± 10 mV SCE respectively. The measured mixed potentials showed an initial decrease of less than 20 mV and recovered rapidly to the free corrosion potential and remained sensibly constant.

A rise in temperature clearly would increase the rate of electrochemical reactions, as well as mass transport by diffusion. Consequently equilibration would be completed in shorter times. The expected temperature dependence is consistent with the observed rate of current decay. These transients also suggest that the reactions of bare steel (or iron) surfaces with the electrolyte involved more than one step. The initial decay is tentatively identified with the charge redistribution that is associated with the evolution of a "double layer". The other steps represented the various electrochemical reactions involving iron, which remain to be identified.

The amount of charge transferred during these reactions can be obtained by numerical integration of the current transients, and are presented in Figure 4. A comparison can be made between this charge transfer and corrosion fatigue crack growth data in accordance with a model proposed by Wei.²⁹ According to this model, the rate of corrosion fatigue crack growth is controlled by the kinetics of the electrochemical reactions, and the cycle dependent component of crack growth rate is proportional to the

amount of hydrogen produced by these reactions during each cycle, and hence to the amount of charge transferred per cycle. The comparison is made, therefore, by matching the charge transfer versus time data directly against the crack growth rate versus equivalent time ($1/\text{frequency}$) results as illustrated in Figure 5. The figure shows good correlation between the charge transfer data at 296 K (23 C) and the published room-temperature corrosion fatigue crack growth rate data for two high strength steels in deaerated 0.6 M NaCl solution.^{30,31} The two sets of data differ by a multiplicative constant, or constant of proportionality, which reflects the unknown surface areas in the two experiments and the amount of hydrogen required to produce each unit area of new crack surface.

It is to be noted that because of the large ratio of cathode-to-anode surface areas (250:1), the mixed potential during the reactions remained essentially constant and was within 20 mV of the free corrosion potential. Thus similar results can be expected if the experiment had been carried out under potentiostatic control at the free corrosion potential. It is anticipated, therefore, that the test procedure can be readily adapted for measuring electrochemical reaction kinetics under potentiostatic conditions. Further examinations of this procedure are in progress.

Although the pH in an occluded cell could be quite alkaline for a freely corroding steel in 0.6 M NaCl solution^{32,33}, neutral solutions were used in these initial simulation experiments principally for simplicity. Furthermore, because of the pumping

action of the fatigue crack, the crack tip environment may reflect that of the bulk electrolyte.

The preliminary evidence, nonetheless, tends to support the hypothesis for electrochemical reaction control of corrosion fatigue crack growth, and suggests that this in situ fracture technique would be effective in providing measurements of the kinetics of the relevant electrochemical reactions. It is recognized that detailed interpretation of data in terms of the underlying reaction mechanisms is still needed, and would require the use of complementary techniques. Additional tests are also needed and are planned to investigate the effects of key electrochemical variables, and to confirm the correlation between electrochemical reaction kinetics and crack growth response over a broader range of environmental conditions.

Summary

An in situ fracture technique has been developed for measuring the kinetics of electrochemical reactions with bare surfaces. Preliminary measurements have been obtained on a steel in deaerated 0.6 M NaCl solution under free corrosion. The measured charge transfer data correlated well with the data on corrosion fatigue crack growth. This correlation indicates the potential of this technique in advancing the understanding of corrosion fatigue in aqueous environments. Additional experiments have been initiated to investigate the effects of key electrochemical variables, and to further confirm the correlation between electrochemical reaction kinetics and crack growth response over a

broader range of environmental conditions.

Acknowledgment

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Figure Captions

- Figure 1: Schematic illustration of the electrochemical cell.
- Figure 2: Galvanic current transients for W1 steel in deaerated 0.6 M NaCl solution as a function of temperature.
- Figure 3: Variation of mixed potentials (measured without IR compensation) with time at three temperatures.
- Figure 4: Amount of charge transferred corresponding to the galvanic current transients in Figure 2.
- Figure 5: Influence of frequency and temperature on fatigue crack growth for HY130 and X70 steels in deaerated 0.6 M NaCl solution.^{30,31} Solid line represents the charge transfer data at 296 K from Figure 4.

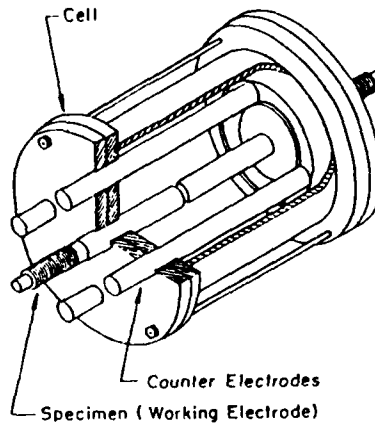


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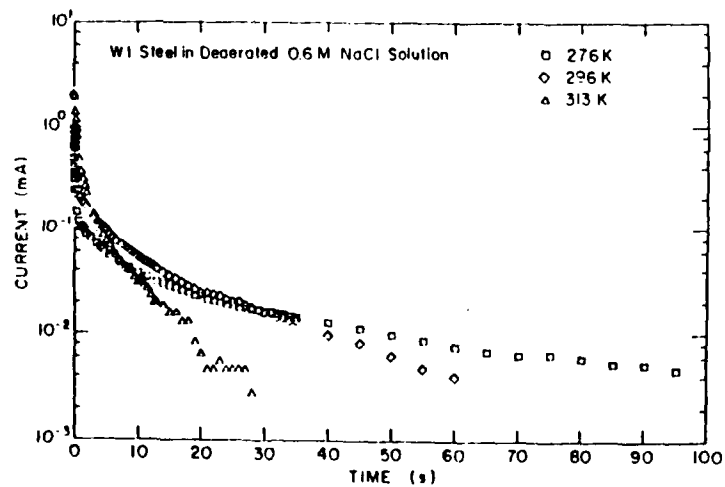


Figure 2: Galvanic current transients for W1 steel in deaerated 0.6 M NaCl solution as a function of temperature.

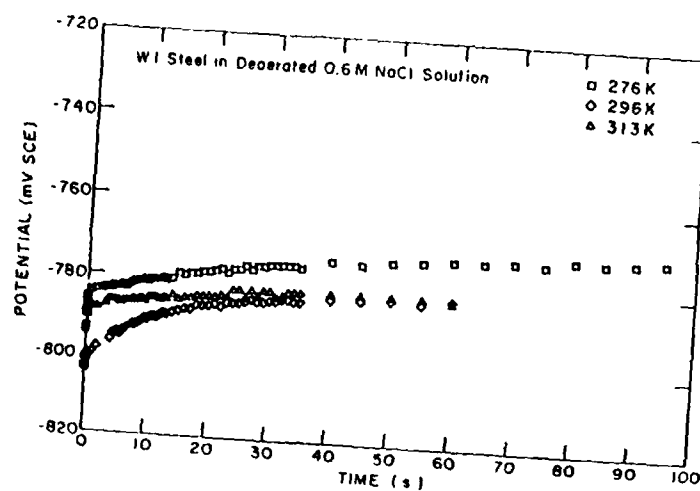


Figure 3: Variation of mixed potentials (measured without IR compensation) with time at three temperatures.

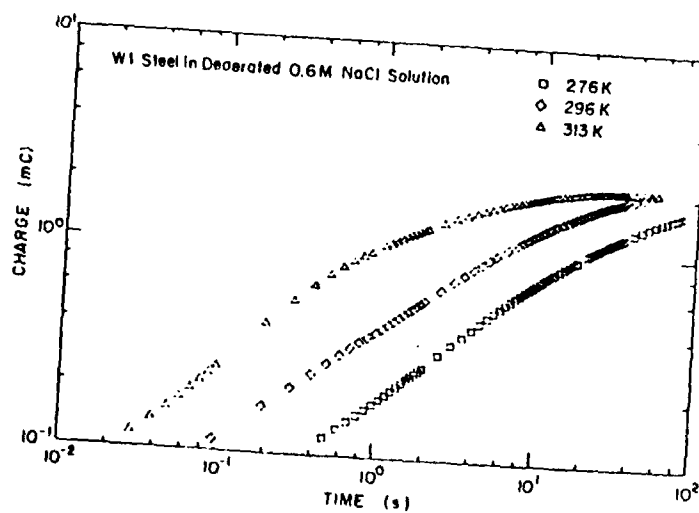


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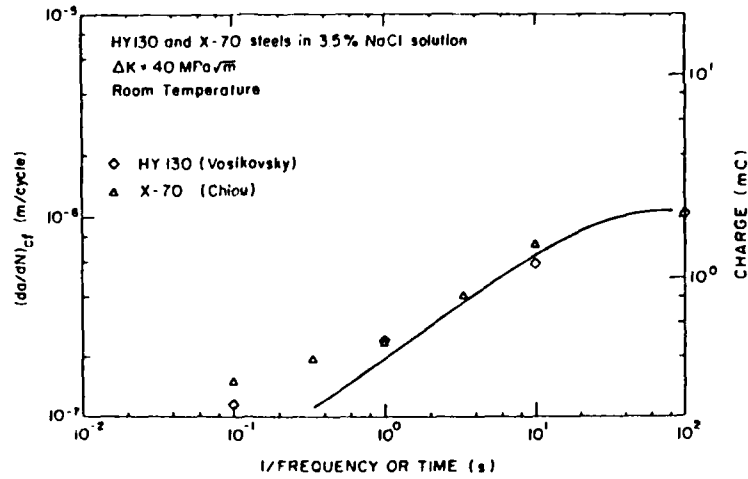


Figure 5: Influence of frequency and temperature on fatigue crack growth for HY130 and X70 steels in deaerated 0.6 M NaCl solution.^{30,31} Solid line represents the charge transfer data at 296 K from Figure 4.

CORRELATION BETWEEN ELECTROCHEMICAL REACTIONS WITH BARE
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Introduction

To determine the relationship between electrochemical (EC) reactions and corrosion fatigue (CF) crack growth for steels in aqueous environments, a new experimental technique has been developed to provide quantitative information on the kinetics of the EC reactions occurring at a bare (fresh) metal surface [1]. This note describes preliminary evidence that supports a direct connection between the extent of EC reactions occurring at a bare surface and the CF crack growth response. The evidence consists of (i) exploratory data on transient EC reactions of bare steel surfaces with deaerated 0.6M NaCl solution, as a function of time and temperature, and (ii) published data on fatigue crack growth rates of several steels in 0.6M NaCl solution as a function of frequency, and of HY-130 steel in deaerated acetate buffer solution as a function of frequency and temperature [2-5].

Background

The correlation between CF crack growth in steels and electrochemical reactions is examined through comparisons of the frequency dependence of the fatigue crack growth rates against the extent of EC reactions as a function of time at different temperatures. The working hypothesis is that crack growth enhancement results from embrittlement by hydrogen, supplied from the EC reactions at the crack tip, and that the crack growth response is governed by the rates of these reactions [6]. This hypothesis is based on previous studies [7,8] and on observed crack growth response [6,9].

The CF crack growth rate data are interpreted in terms of a superposition model [10], where the cycle dependent component of the measured crack growth rate, $(da/dN)_{cf}$, for different frequencies and temperatures, is given by Eqn. (1):

$$(da/dN)_{cf} = (da/dN)_e - (da/dN)_r = [(da/dN)_c - (da/dN)_r] \phi \quad (1)$$

In Eqn. (1), $(da/dN)_e$ = measured crack growth rate; $(da/dN)_r$ = mechanical fatigue crack growth rate; $(da/dN)_c$ = "pure" CF crack growth rate; and ϕ = fractional area of crack undergoing "pure" CF, with $0 < \phi \leq 1$. (To simplify notations, $(da/dN)_c$ is used here in place of $(da/dN)_{cf,s}$ in [10].) The quantity ϕ can be equated with the extent of reactions of the environment with the crack-tip surfaces (or the fractional surface coverage θ) per load cycle [11]. Both $(da/dN)_c$ and $(da/dN)_r$ are essentially independent of the cyclic load frequency, and are only mildly dependent on temperature [11]. The principal effects of frequency and temperature on CF crack growth are expected to be reflected through their influences on ϕ , or θ .

The extent of surface reaction per load cycle, θ and hence ϕ , is identified with the fractional amount of electric charge transferred, (q/q_s) , by the reactions of newly formed crack surfaces with the electrolyte at the crack tip. The amount of hydrogen produced each cycle is assumed to be directly proportional to the amount of charge transferred (q), which is governed by the reaction time and by the rates of reactions. Temperature, through its influence on reaction rates, affects the amount of charge transferred in a given time. The maximum or "saturation" level of charge (q_s) represents the amount required to complete the surface reactions and is expected to be independent of temperature if the reaction mechanisms remain unchanged.

Based upon the foregoing hypothesis, there should be a direct correlation between the fractional area of crack undergoing "pure" CF, ϕ , (or CF crack growth rate $(da/dN)_{CF}$) and the fractional amount of charge transferred, (q/q_s) . For the CF data, with positive load ratios, the period of the loading cycle (or the inverse of cyclic loading frequency, $1/f$) is taken to be the equivalent reaction time [11]. The charge transfer data are obtained independently from a recently developed experimental technique [1]. Using this technique, the transient galvanic current between an electrode, fractured in-situ, and oxidized electrodes (simulating that occurring between the crack tip and the crack flank) is measured as a function of time and temperature. The amount of electric charge transferred versus time is then obtained by numerical integration of the current transient and is used for comparisons with the fatigue data.

Results and Discussion

Electrochemical experiments were performed on a W1 (C-Mn) tool steel in deaerated, 0.6M NaCl solution (pH 6.5), under freely corroding (or open circuit) conditions, at three temperatures [1]*. Exploratory data from these experiments are shown in Fig. 1 as a plot of (q/q_s) versus time at the different temperatures. The charge transfer is normalized with respect to q_s to minimize scatter introduced by small differences in fracture surface area and roughness. With increases in temperature, the (q/q_s) curve is seen to translate to the left, or to shorter times. This shift reflects an increase in the reaction rate with temperature.

For comparison, CF crack growth data for several steels, tested in 0.6M NaCl solutions (pH 6.4-6.8) at ambient temperature with ΔK values close to 40 MPa/m and low R ratios, are shown in Figs. 2 to 4, along with a curve representing the 296K charge transfer data from Fig. 1. To provide for a preliminary assessment of the effect of temperature, a comparison between (q/q_s) and crack growth data of a HY130 steel in acetate buffer solution (pH 4.2) at three temperatures is made in Fig. 5. It is recognized that the detailed kinetics and mechanisms of reactions, however, may be different. The comparisons are made by vertically shifting the (q/q_s) data against the CF data until a good fit is obtained. The two sets of data are assumed to differ by a multiplicative constant, or constant of proportionality, which reflects the different surface areas between the two experiments and the exact amount of hydrogen required to produce a given increment of corrosion fatigue crack growth. For a more direct comparison, the values of ϕ , calculated using $(da/dN)_C$ values estimated from Figs. 2 to 4, and (q/q_s) at equivalent times are shown against each other in Fig. 6.

Figures 2 through 4 and Fig. 6 show a good correlation between the CF crack growth response and charge transfer ratio data particularly at the lower frequencies (longer times). Figure 5 demonstrates the similarity between the temperature dependence of the two processes.

* Note: This solution and conditions were chosen for simplicity. It is recognized, however, that the crack-tip chemistry may be different, and the influence of these variables on the reaction kinetics require further examination.

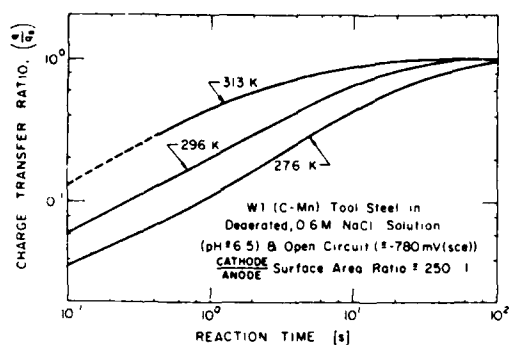


FIG. 1. Charge transfer ratio vs. reaction time of W1 steel at three temperatures[1].

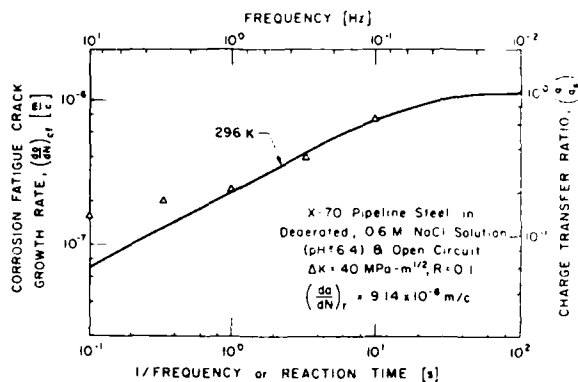


FIG. 2. Correlation of CF data on X-70 steel with (q/q_s) from Fig. 1 [2].

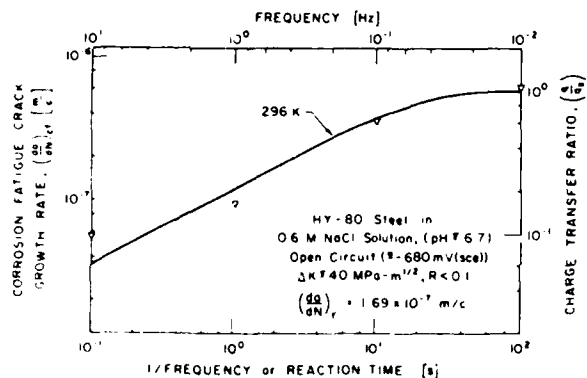


FIG. 3. Correlation of CF data of a HY-80 steel with (q/q_s) from Fig. 1 [3].

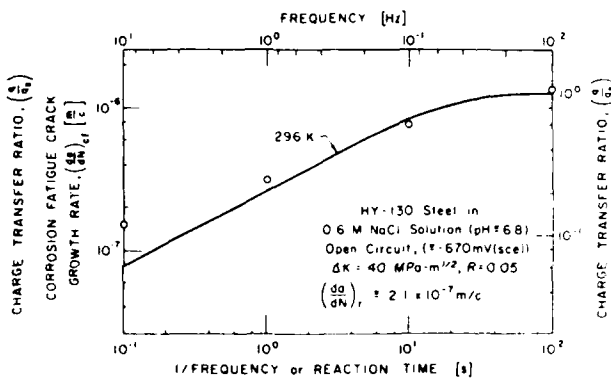


FIG. 4. Correlation of CF data of a HY-130 steel with (q/q_s) from Fig. 1 [4].

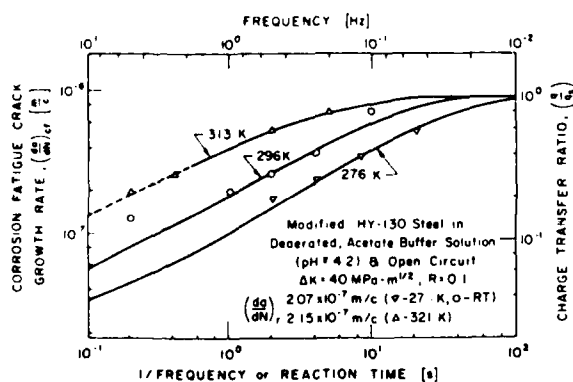


FIG. 5. Comparison of the temperature effect on the CF data of HY-130 steel with (q/q_s) from Fig. 1 [5].

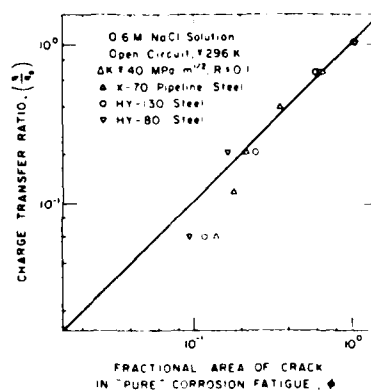


FIG. 6. Comparison of ϕ values taken from Figs. 2-4 with (q/q_s) from Fig. 1.

Two possible reasons may be offered for the discrepancy in the room temperature data for the NaCl solution. Firstly, the corrosion fatigue data are obtained by subtracting off a reference rate from the measured rate (see Eqn. (1)). Because the rates at the higher frequencies approach the reference rate, substantial uncertainty may be introduced and the discrepancy simply reflects the uncertainties introduced by this calculation. Secondly, the process that is responsible for the enhancement of crack growth at the higher frequencies may be the chemisorption of water, and the concomitant production of hydrogen. The chemisorption process may not be electrochemical in nature, and would not be reflected in the charge transfer measurements.

Nevertheless, the correlation is most encouraging and suggests that a fruitful avenue for understanding CF of ferrous alloys in aqueous environments has been opened.

Summary

The results of this preliminary correlation demonstrate the relationship between electrochemical reactions with bare metal surfaces and CF crack growth for steels in aqueous environments, and is very encouraging. These findings provide further support for the hypothesis of surface/electrochemical reaction control, and indicate the effectiveness of the in-situ fracture technique in providing unambiguous measurements of bare-surface reaction kinetics. For quantitative modeling, efforts will be needed to provide measurements of current and charge densities, and to address the issue of actual surface areas of cracks. Additional research is in progress and will be reported.

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